

# Mid-IR and Near-IR *in situ* instrument needs

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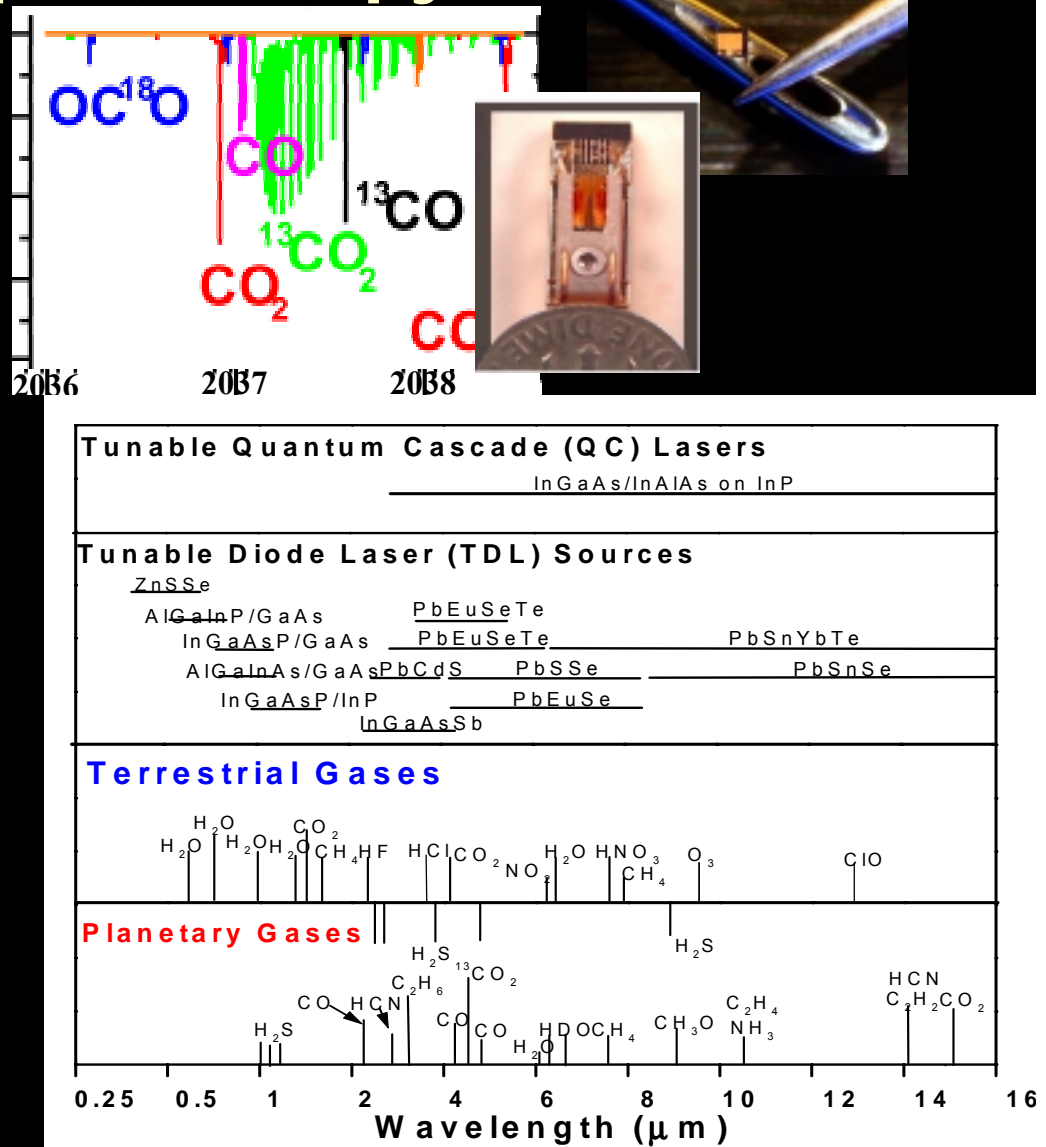
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- Summary of Mid-IR Spectroscopic Measurement Needs



10/30/200

# Laser Absorption Spectroscopy

- **Narrowband ( $0.0005\text{ cm}^{-1}$ ) tunable diode lasers (TDL) and Quantum-cascade (QC) lasers matched to absorption line(s) ( $1.3 - 10\text{ }\mu\text{m}$ ) of gases of interest.**
- **Numerous TDL-based absorption instruments have been flown on balloon & aircraft missions.**
- **For Earth, well-suited to certain target gases:  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$ , isotopes of  $\text{H}_2\text{O}$ , isotopes of  $\text{CO}_2$ .**
- **Sensitivity – sub-parts-per-billion.**



# Overview of Aircraft, Balloon, and Ground-based instruments

~ 30 TDL/QC laser spectrometers currently measuring Earth atmospheric gases

## Laser Sources:

- Near-IR TDLs (InGaAsP) operate cw at room temp (TE cooler)
- Traditional Mid-IR (Pb-salt) TDLs operate at LN<sub>2</sub> temps
- Mid-IR QC lasers (InGaAs) operate cw at LN<sub>2</sub>, pulsed at room temp

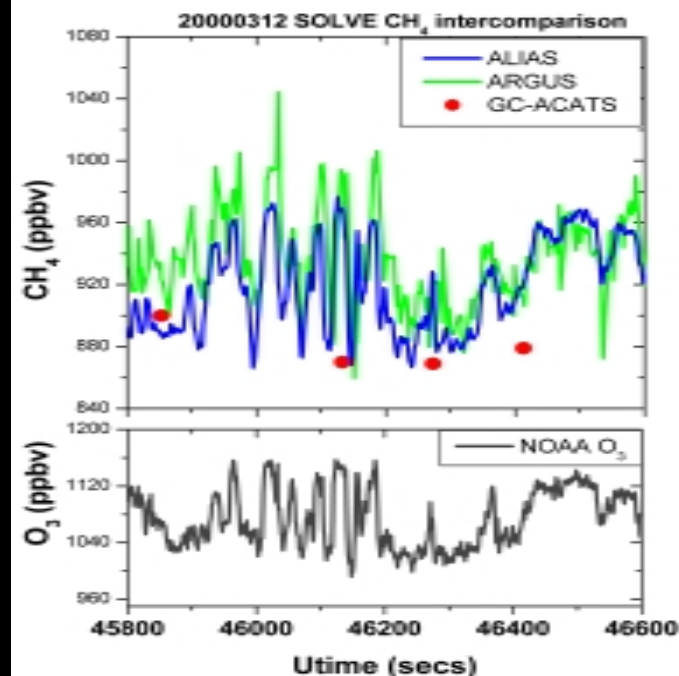
## Measurement Geometry:

- Open path (large  $\Delta T$ ) or flowing cell (T-regulated)

## Technique:

- Line-locked: higher duty cycle (precision), poor line information
- Tunable: full spectral line information, lower duty cycle (precision) [2f or sweep integration]
- LAS and CRDS

Unified N<sub>2</sub>O: GCMS has better absolute accuracy, but laser spectrometers offer superior sensitivity, specificity, precision, and response time.



# Mid-IR Aircraft, Balloon, and Ground-based Spectrometers

Instrument	Path	Technique	PI	Institution	Platform	Gas	Line (cm <sup>-1</sup> )	Calibration	Precision 1 $\sigma$	Accuracy
ALIAS	Flowing Herriott cell 80 m	Tunable TDL and QC	Chris Webster	JPL	ER-2	N <sub>2</sub> O CH <sub>4</sub> CO CO <sub>2</sub> HCl NO <sub>2</sub>	2232 1256 2169 2233 2926 1603	Pre-flight + in-flight CO <sub>2</sub> Pre-flight Pre-flight In-flight CH <sub>4</sub> Pre-flight	0.6% in 1.3 sec 0.3% in 1.3 sec 1% in 1.3 sec (trop) N/A 1% 5%	$\pm$ 1.8% $\pm$ 3% $\pm$ 3% N/A 3% 5%
ALIAS-II	Open path Herriott cell 64 m	Tunable	Chris Webster	JPL	Balloon	N <sub>2</sub> O CH <sub>4</sub> HCl	2237.7 2927.1 2925.9	Pre-flight Pre-flight In-flight CH <sub>4</sub>	3% 3% 10%	$\pm$ 5% $\pm$ 5% $\pm$ 10%
ALIS	Flowing Herriott cell 2.8 m	Tunable QC	Chris Webster	JPL	WB-57F	<sup>13</sup> CO <sub>2</sub> CO <sub>2</sub>	2303	In flight	0.1% for line ratio in 1.3 sec	Isotopic ratio
ARGUS	Flowing Herriott cell	Tunable	Max Loewenstein, Hansjurg Jost	NASA Ames	ER-2 Balloon	N <sub>2</sub> O CH <sub>4</sub>	2206 3028	In-flight	1.5% in 2 sec	3.5% in 2 sec
ATLAS	Flowing White cell	Line-locked	Max Loewenstein, Jim Podolske	NASA Ames	ER-2	N <sub>2</sub> O	2232	In-flight	about 0.1%	1% 1 $\sigma$
BLISS	Open path 0.3-1 km (Lowered retro)	Tunable	Chris Webster	JPL	Balloon	HCl N <sub>2</sub> O CH <sub>4</sub> CO NO <sub>2</sub> NO HNO <sub>3</sub> O <sub>3</sub>	2926 1252 1343 2169 1603 1900 1333 1063	Spectroscopic line parameters	1-5% in 30 sec	2-15%
DACOM I	Flowing cell 36 m Herriott Cell	Line-locked	Glen Sachse	NASA LaRC	DC-8	CO CH <sub>4</sub> N <sub>2</sub> O	2116 $\pm$ 3018 $\pm$ 2212 $\pm$	In-flight NOAA/CMDL Standard	1% in 1 sec 0.1% in 1 sec 0.1% in 1 sec	2% 1% 1%
DACOM II	Flowing cell 36 m Herriott Cell	Line-locked	Glen Sachse	NASA LaRC	P-3	CO CH <sub>4</sub>	2116 $\pm$ 3018 $\pm$	In-flight NOAA/CMDL Standard	1% in 1 sec 0.1% in 1 sec	2% 1%
FLAIR	Flowing White cell 126 m	Line-locked and 2f	G.W. Harris	York Univ. Canada, MPI Germany.	F-116	H <sub>2</sub> O <sub>2</sub> NO <sub>2</sub> HCHO CO	1245 1629 1730 2073	Pre-flight?	Xx% in 1 minute?	??????
NERC IFMA spectrometer	Open path	Tunable	Howieson, Duxbury, Swann, Gardiner, Jones	Strathclyde U., NPL, & Cambridge U., UK	Balloon 5-30 km	CH <sub>4</sub>	6097	??????	??????	??????

# Mid-IR Aircraft, Balloon, and Ground-based Spectrometers (contd.)

Instrument	Path	Technique	PI	Institution	Platform	Gas	Line (cm <sup>-1</sup> )	Calibration	Precision 1 $\sigma$	Accuracy
NERC COSMAS NIR	Flowing cell or open path	Tunable	Walker, Langford, Duxbury, Brassington	Strathclyde U., & Imperial College, UK	Ground or aircraft	C <sub>2</sub> H <sub>6</sub> CH <sub>4</sub> CH <sub>3</sub> OH H <sub>2</sub> CO	6097 1730		TBD	TBD
NCAR TDLAS	??????	??????	Bill Mankin and Mike Coffey	NCAR	WB-57 C-130	CO, N <sub>2</sub> O	??????	??????	3% in 30 sec	5%
NOAA TDLAS	??????	??????	Eric Richards, Ken Kelly	NOAA	WB-57	CH <sub>4</sub>	??????	??????	??????	5%
OPTIMA	Open path Herriott cell	Rapid Scan HF 2f	Jim Podolske	NASA ARC	DC-8	HNO <sub>3</sub>	1721-1723	Absolute spectral parameters	TBD	TBD
Cavity Ringdown Laser Spectrometer	??????	??????	Jim Anderson	Harvard University	WB-57F	CH <sub>4</sub>	1333	Pre-flight + in-flight gas addition	0.3% for 10 sec	1%
Eddy - Correlation TDLAS	Flowing cell (Herriott)	Dewar based, tunable system with line locking	Peter Werle and Robert Korman	Fraunhofer Institute, Germany	Ground	CH <sub>4</sub>	1290	Calibration Gas from cylinder + dilution system (every 30 min)	0.5% for 0.1 sec	??????
TDLAS for formaldehyde	Flowing Astigmatic Herriott cell	Tunable, 2f + sweep integration	Alan Fried	NCAR	Ground, DC-8, Electra, WP3, C-130	HCHO	2831.6417	In flight calibration and zeroing	20 - 50 pptv in minute (1 $\sigma$ ), 150 - 400 pptv in 1 second	6 - 10 %
Mid infrared TDLAS	Flowing cell (White)	Tunable system with line locking	Peter Werle et al.	Fraunhofer Institut, Germany	Ground	NO <sub>2</sub>  CH <sub>4</sub>  HCOH	1600  3076  2800	Permeation System  Calibration Gas  Permeation System	0.3% for 1.5 sec 0.08% for 25 sec 0.3% for 1.5 sec 0.08% for 25 sec 2% for 0.06 sec 0.5% for 1 sec 0.1% for 20 sec 1.4% for 1.5 sec 0.3% for 40 sec	??????
TDLAS	??????	??????	Harold Schiff	??????	Electra	NO <sub>2</sub> HNO <sub>3</sub>	??????	??????	??????	??????
TDLAS	Flowing White cell	??????	Don Hastie and Miller	??????	Balloon	NO, NO <sub>2</sub>	??????	??????	??????	??????
TILDAS-36 TILDAS-200	Flowing path	Tunable, direct absorption	Mark Zahniser	Aerodyne Research Inc	Ground  Flux Tower  Mobile van	CH <sub>4</sub> N <sub>2</sub> O HNO <sub>3</sub> NO <sub>2</sub> NO SO <sub>2</sub> NH <sub>3</sub>	3017 2240 1722 1600 1900 1370 1065	Cal gas Cal gas HITRAN line parameters  JPL lines	0.1% in 1 sec 0.1% in 1 sec 500 ppt 1 sec 200 ppt 1 sec 500 ppt 1 sec 500 ppt 1 sec 100 ppt 1 sec	$\pm$ 5% $\pm$ 5% $\pm$ 20% $\pm$ 20% $\pm$ 20% $\pm$ 20% $\pm$ 20%

# Near-IR Aircraft and Balloon Spectrometers

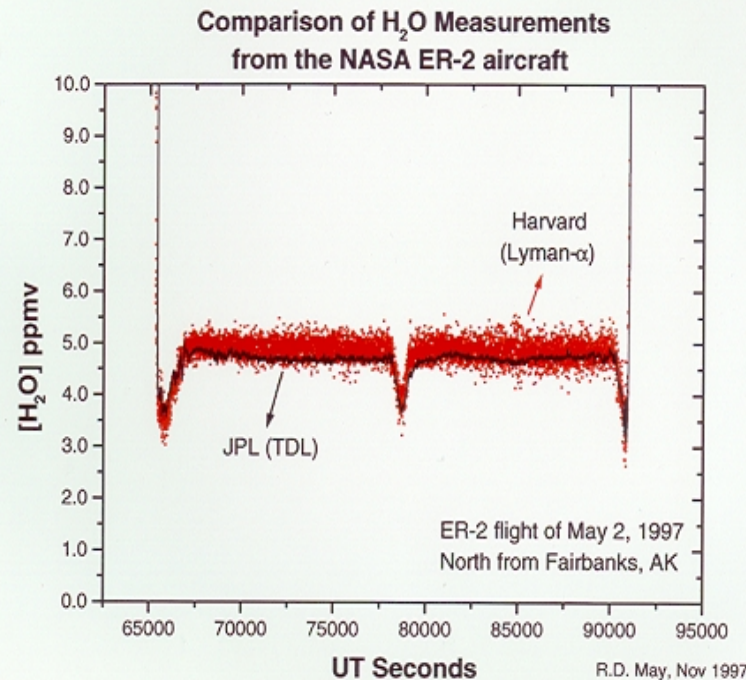
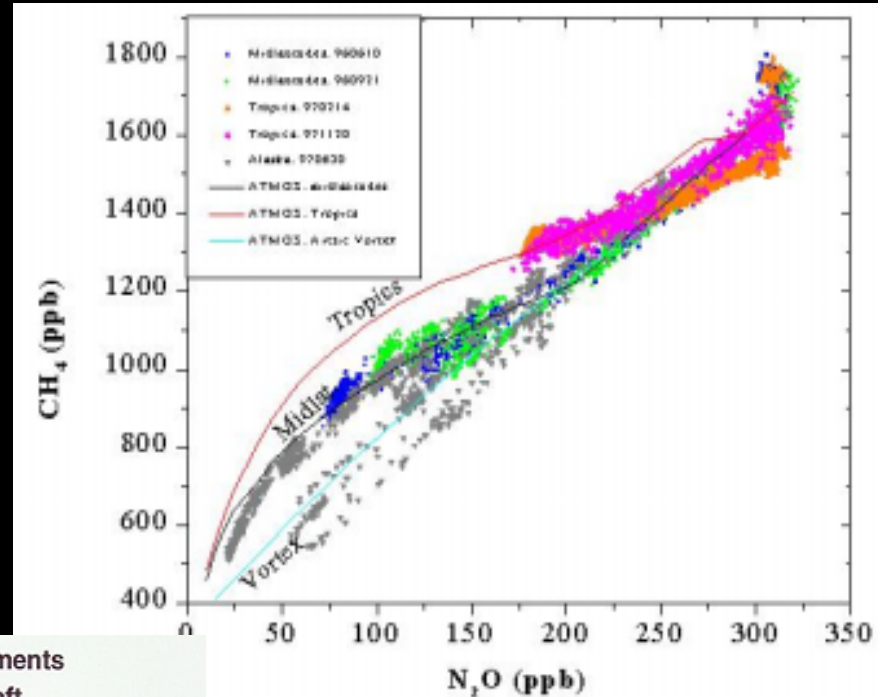
Instrument	Path	Technique	PI	Institution	Platform	Gas	Line (cm <sup>-1</sup> )	Calibration	Precision 1 $\sigma$	Accuracy
DLH	30m Open path	Line locked	Glenn Sachse Jim Podolske	NASA LaRC/Ames	DC-8	H <sub>2</sub> O	7118 and 7122	Pre and post mission	Greater of 0.1 ppmv or 2% conc. in 50 msec	10%
JLH-ER-2	Open path	Tunable	Bob Herman	JPL	ER-2	H <sub>2</sub> O	7294.1	Pre-flight	1-2% in 1 sec	± 5%
JLH-WB57	Open path	Tunable	Bob Herman	JPL	WB57	H <sub>2</sub> O	7299.4	Pre-flight	1-2% in 1 sec	± 5%
JLH-DC-8	Open path	Tunable	Bob Herman	JPL	DC-8	H <sub>2</sub> O	7306.8	Pre-flight	???????	???????
NCAR Water	Open path	Tunable	Bruce Gandrud	NCAR	C-130	H <sub>2</sub> O	???????	???????	???????	???????
Physical Sciences LH	Open path	Tunable, Balanced ratiometric detection	David Sonnenfroh	Physical Sciences, Inc.	P3 B	H <sub>2</sub> O	7181.2	???????	???????	???????
SDLA	Open path	Tunable	Georges Durry	CNRS, France	Balloon	CH <sub>4</sub> , H <sub>2</sub> O	6046.9, 7181.1(strat) 7188.3(trop) 7185.6(trop) 7183(trop)	Pre-flight	???????	5%-10%
SWS LH	Open path	Tunable	Joel Silver, DC Hovde	Southwest Sciences, Inc	KC-135	H <sub>2</sub> O	7612	???????	???????	???????
Near infrared TDLAS	Flowing cell (Herriott)	Peltier cooled, tunable system with line locking	Peter Werle et al.	Fraunhofer Institut, Germany	Ground	CO <sub>2</sub>	4990	Calibration Gas	0.08% for 1 sec	???????
TOTCAP Water	Flowing path	Tunable	Linnea Avallone	LASP/ U.Colorado	DC-8, commercial	H <sub>2</sub> O	7306.75	Pre-flight and post flight	1-2% in 1 sec	5%-10%



- Increasingly-sophisticated scientific questions addressed by *in situ* payloads (aircraft, balloon) has increased demand for higher precision, higher accuracy measurements of tracers, water.

(e.g. CO<sub>2</sub> vs. N<sub>2</sub>O tracer correlations)

- Aircraft platforms have duplication with differing techniques for continuous intercomparison.



# IR Vibration-rotation Lineshapes

Linestrength is integrated absorption coefficient

$$S = \int k(\tilde{\nu}) d(\tilde{\nu})$$

$$k(\tilde{\nu}) = S g(\tilde{\nu} - \tilde{\nu}_o)$$

Natural linewidths ~tens of kHz (msec lifetimes)

• Doppler Line Broadening

$$\gamma_D \text{ directly } \propto T^{1/2}$$

$$= 3.581 \times 10^{-7} \nu_0 (T/M)^{1/2} \text{ cm}^{-1} (\sim \text{tens of MHz})$$

$$k(\tilde{\nu}) = \left( \frac{S}{\gamma_D} \right) \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left[ -(\tilde{\nu} - \tilde{\nu}_o) \ln 2 / \gamma_D^2 \right]$$

• Collisional Line Broadening

$$\gamma_L \propto 1/T^{1/2}$$

$$g_L(\tilde{\nu} - \tilde{\nu}_o) = \frac{\left( \frac{\gamma_L}{\pi} \right)}{(\tilde{\nu} - \tilde{\nu}_o)^2 + \gamma_L^2}$$

$$\gamma_L = \left[ \gamma_A \left( \frac{P_a}{P_0} \right) + \gamma_B \left( \frac{P_b}{P_0} \right) \right] \left( \frac{T_o}{T} \right)^s$$

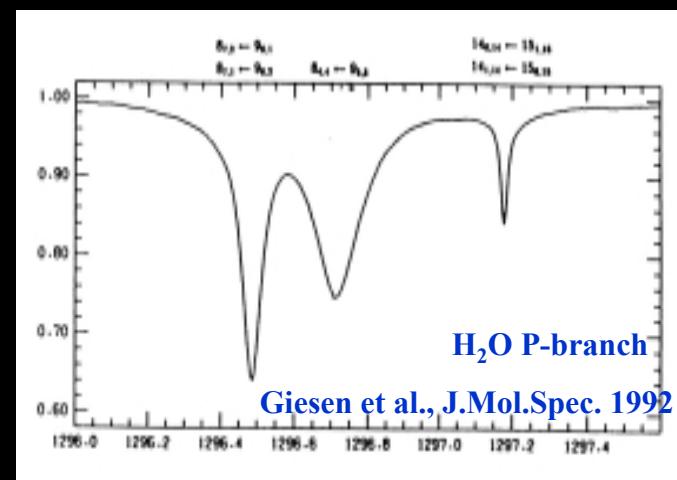
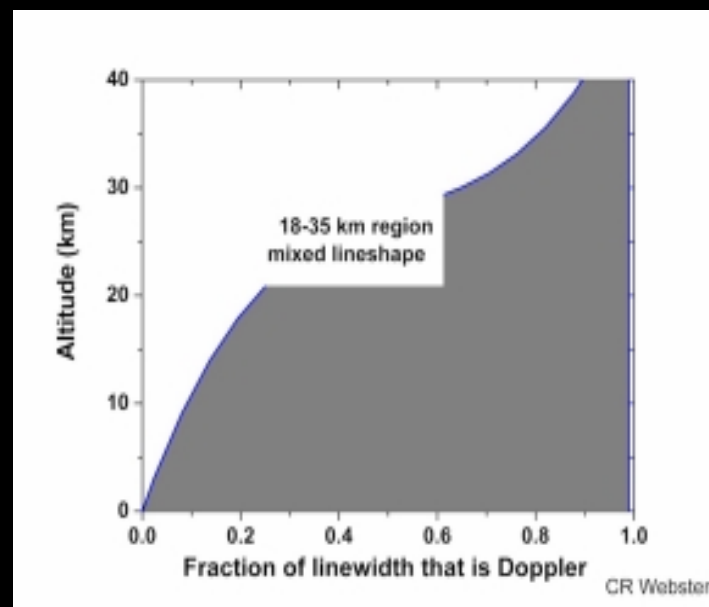
SBC > FBC SBC=0.08 cm<sup>-1</sup> atm<sup>-1</sup>(CH<sub>4</sub>) to 1.0 (HNO<sub>3</sub>)

FBC up to 0.15 cm<sup>-1</sup> atm<sup>-1</sup> for N<sub>2</sub> on H<sub>2</sub>O

Width usually varies smoothly with m.

Mixed Lineshapes and the Voigt Profile

• Pressure-broadening coefficients of H<sub>2</sub>O known to depend on rotational quantum numbers of vib-rot transitions involved, but not always temp dependence (0.6-0.8) [Varanasi]



# Spectroscopic needs for *in situ* laser spectrometers

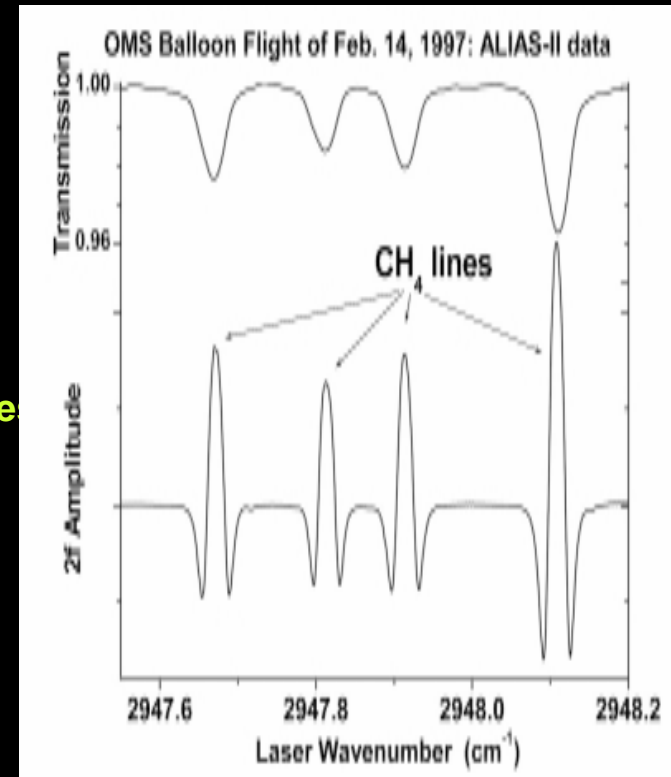
- Spectroscopic needs are fundamentally different from those of remote sensing spectrometers.

- Care about behavior of carefully-chosen, isolated, single lines:

- absolute line strength (precision)
- $E''$  (temperature change or extrapolation susceptibility)
- broadening coefficient and temp dependence (extrapolation linearity)
- temperature dependence of line shape to avoid surprise in modulation methods
- interferences (esp. for weak lines of  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_3$  etc.)
- Pressure-shifts for instruments line-locked to fixed reference cell pressure.

- For known spectroscopic parameters, absorption method is self-calibrating through Beer's Law.

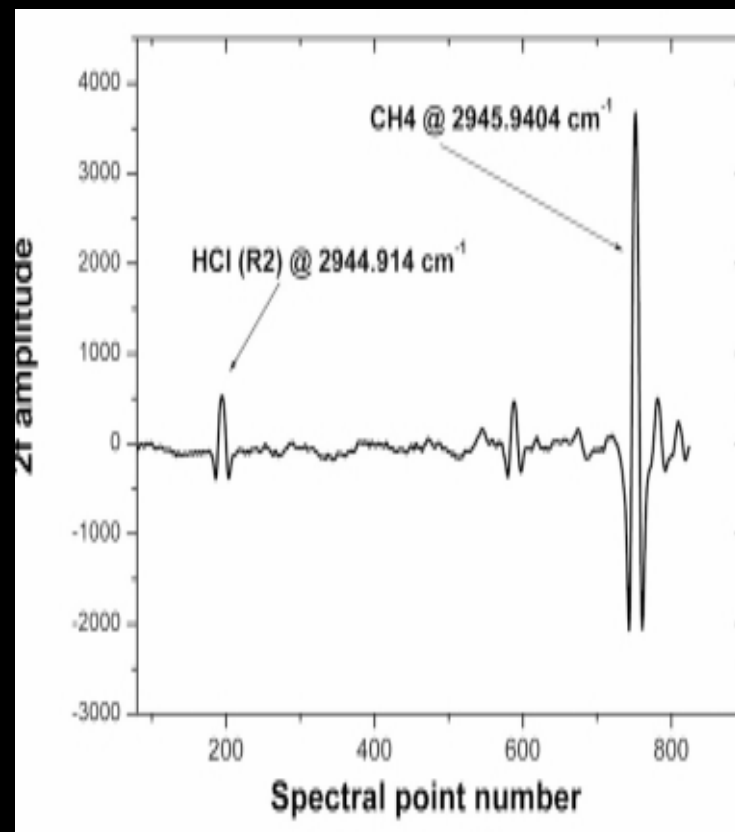
- Need path length, laser line-width (Doppler cells), pressure, temperature, direct absorption spectrum.



# Calibration methods for *in situ* laser spectrometers

## REACTIVE GASES

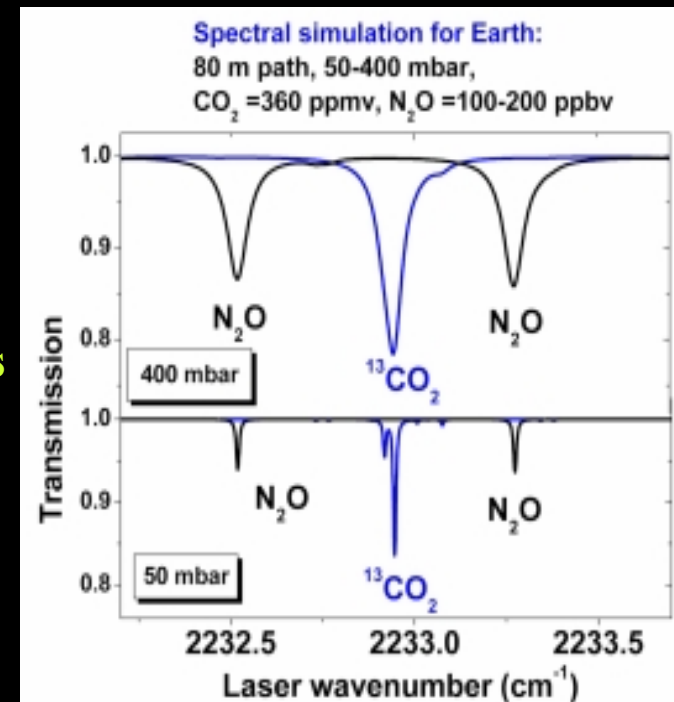
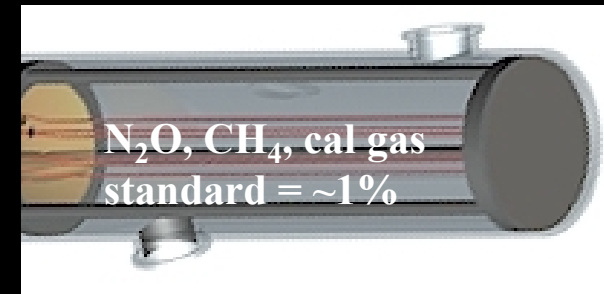
- Chemically, thermally, or photochemically unstable in reference gas cells
- Pre-flight calibration difficult (especially at low Temps and low mixing ratios:
  - sticky (polar) molecules:  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$
  - $\text{NO}$ ,  $\text{NO}_2$  permeation tubes
  - $\text{H}_2\text{CO}$  (Alan Fried) uses Henry's Law Calibration System HLCS
  - $\text{H}_2\text{O}$  laser spectrometers use chilled-mirror frost-point hygrometer
- Rely on spectroscopic line parameters that limit measurement uncertainty to ~5-10%
- Use adjacent line normalization where possible (e.g.  $\text{CH}_4$  for  $\text{HCl}$ )



# Calibration methods for *in situ* laser spectrometers (contd.)

## STABLE GASES

- **Pre-flight calibration using gas standards (~1%)**
  - Referenced to NIST or CMDL standards
  - Easy to map pressure dependence
  - Very difficult to map temp dependence
- **In-flight switching to reference gas cells**
  - Need to be same pressure and temp as sampled atmosphere
- **In-flight calibration using reference atmospheric gas lines such as CO<sub>2</sub>**
  - Even seasonal cycle variation in CO<sub>2</sub> is only  $\pm 1.4\%$
  - But still limited by pressure broadening parameters



# Measurements of Atmospheric Tracers

## $N_2O$ , $CH_4$ , $CO$

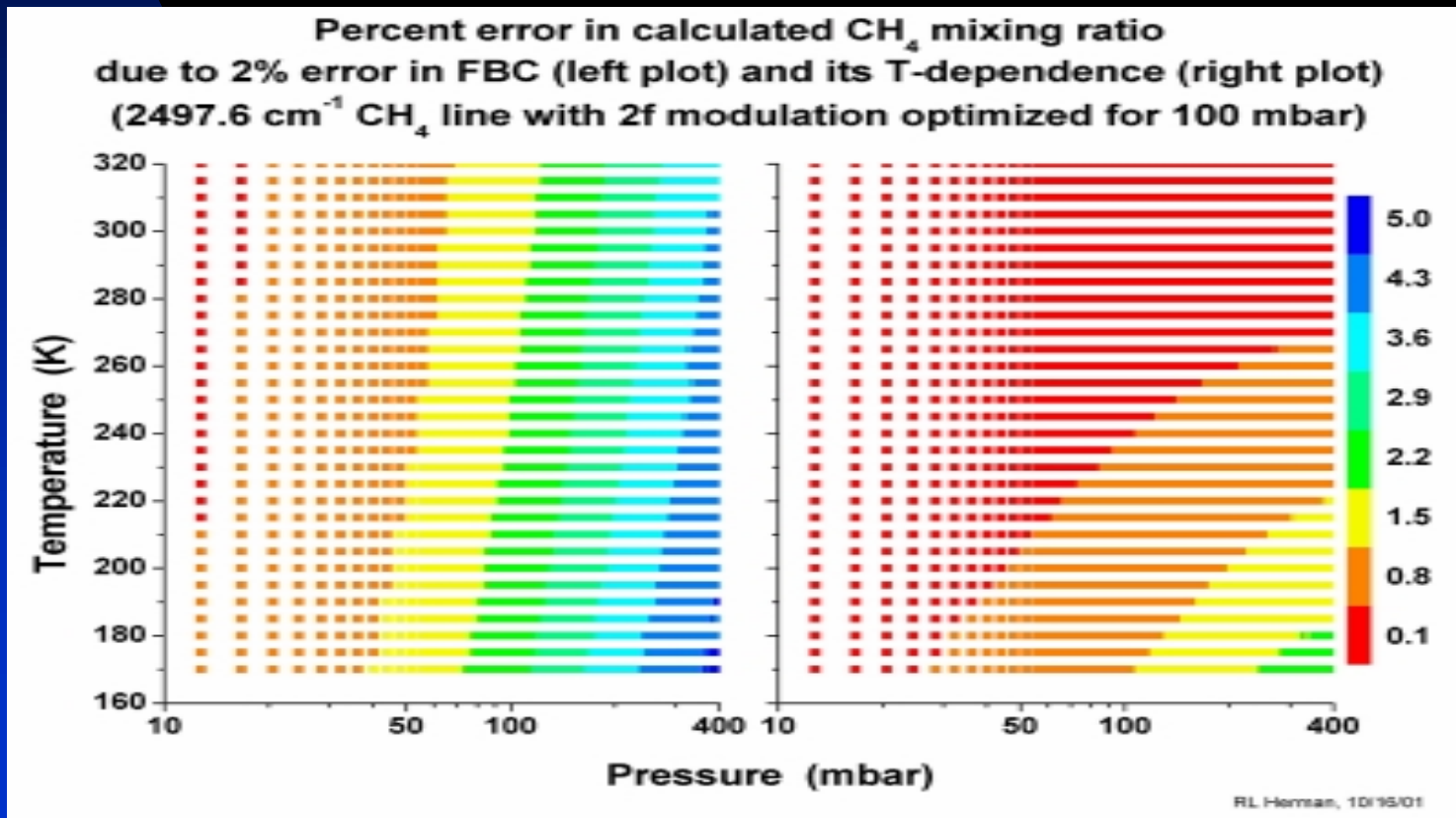
	<u>BAND</u>	<u>UNCERTAINTY</u>		
		<u>Line strengths</u>	<u>FBC</u>	
<u>Strong N<sub>2</sub>O bands:</u>				
~4.5 μm (2200 cm <sup>-1</sup> )	v <sub>3</sub>	3%	4%	smooth FBC, S, n, with m: (Fukabori, Varanasi)
~7.7 μm (1300 cm <sup>-1</sup> )	v <sub>1</sub>	3%	4%	
<u>Strong CH<sub>4</sub> bands:</u>				
~3.3 μm (3000 cm <sup>-1</sup> )	v <sub>3</sub>	1-2%	2-5%	some differences, line mixing (Fukabori)
~7.7 μm (1300 cm <sup>-1</sup> )	v <sub>4</sub>	2-5%	2-5%	
~2.3 μm (4350 cm <sup>-1</sup> )	v <sub>3</sub> + v <sub>4</sub>	2-5%	2-5%	
<u>Strong CO bands:</u>				
~4.8 μm (2100 cm <sup>-1</sup> )	fund.	2-5%	5-10%	series var. of n 0.6-0.8 with m (Varanasi)
[~2.4 μm band (near-IR) too weak for stratosphere]				



# Measurements of Atmospheric Tracers $\text{N}_2\text{O}$ , $\text{CH}_4$ , $\text{CO}$ (contd.)

For typical aircraft data altitudes (50-300 mbar)

- 2% error in FBC results in ~2% error in final mixing ratio
- 2% error in  $n$  results in ~1% error in final mixing ratio



# Atmospheric Measurements of H<sub>2</sub>O



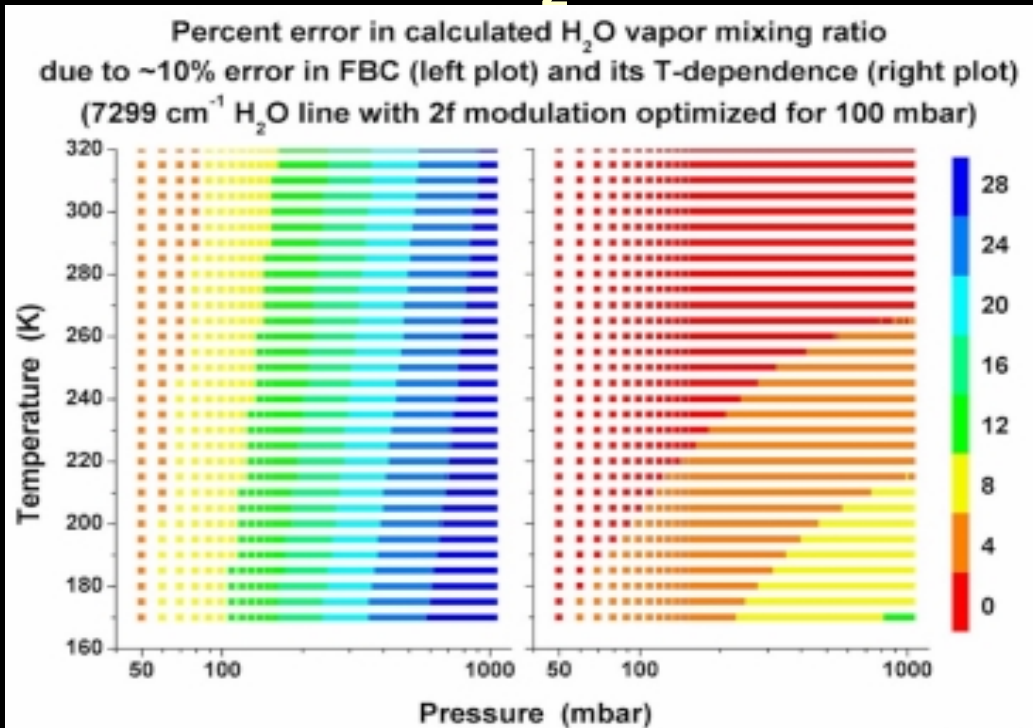
**Minimum-detectable mixing ratio for 10 meter path length and  $2 \times 10^{-5}$  absorptance:**

- Mid-IR is 20 times stronger than near-IR at 1.37  $\mu\text{m}$ 
  - 30 parts-per-billion at 1.37  $\mu\text{m}$  (in 1 sec)
  - 1.5 parts-per-billion at 5.9  $\mu\text{m}$
- Near-IR TDLs available at room (TE cooler) temperatures, and InGaAs detectors are excellent.
- Mid-IR QC lasers will eventually dominate and offer much shorter pathlengths, smaller instruments.



# Near-IR Measurements of H<sub>2</sub>O

- Unlike other gases,  $\text{H}_2\text{O}$  mixing ratios span 4 orders of magnitude from trop to strat.
- Usually calibrate with chilled-mirror frost-point hygrometer at room temp.
- For diff temperatures, extrapolation is necessary.
- Accuracy in FBC (esp.) and its' T dep is critical.



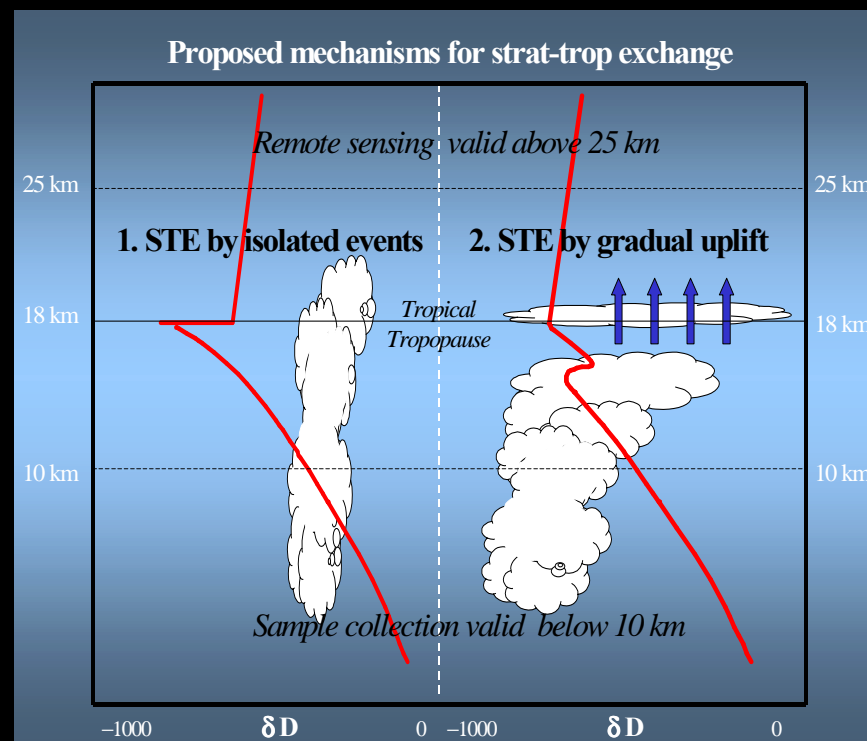
91. Herrero, 12/18/07

[illegible]

# Measurements of Water Isotopes

## $\text{H}_2\text{O}$ , $\text{HDO}$ , $\text{H}_2^{18}\text{O}$ , $\text{H}_2^{17}\text{O}$

- Determine the processes that regulate upper tropospheric (UT) water vapor, and its' transport into the lower stratosphere (LS).
- Does Strat-Trop Exchange occur through isolated deep convection in the tropics, or gradual uplift of high cirrus or ice sublimation?
- $\text{HDO}$  preferentially partitioned into the condensed phase:  $\text{HDO}/\text{H}_2\text{O}$  decreases rapidly to top of convective system.
- $\delta\text{D}$  ( $\text{HDO}$ ) changes by large amount (tens of %).
- If adjacent isotopic lines used, precision more important than accuracy.



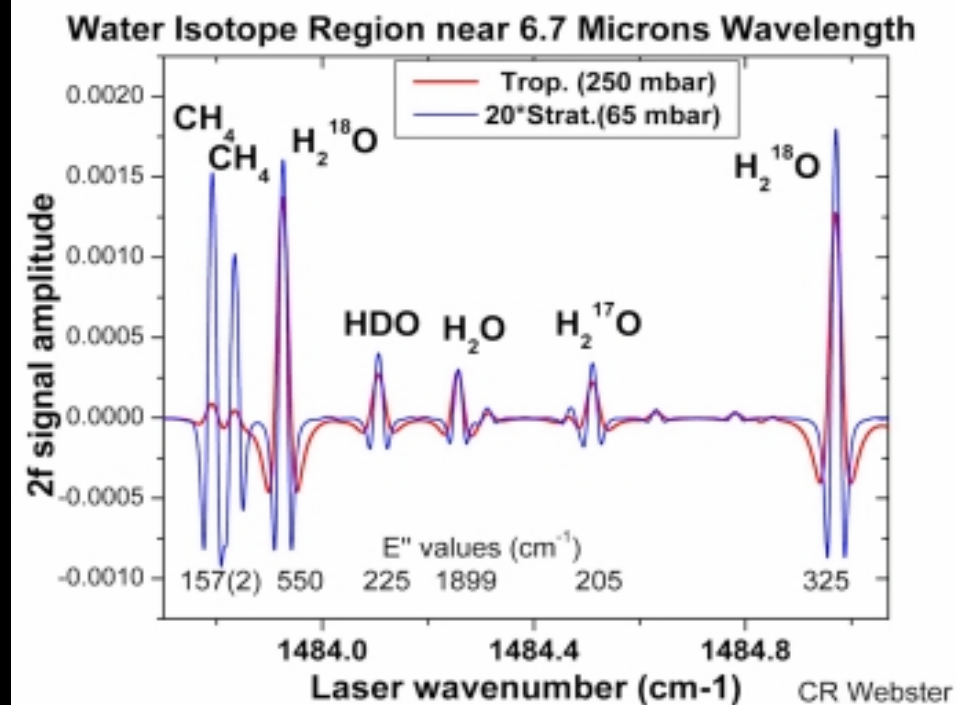
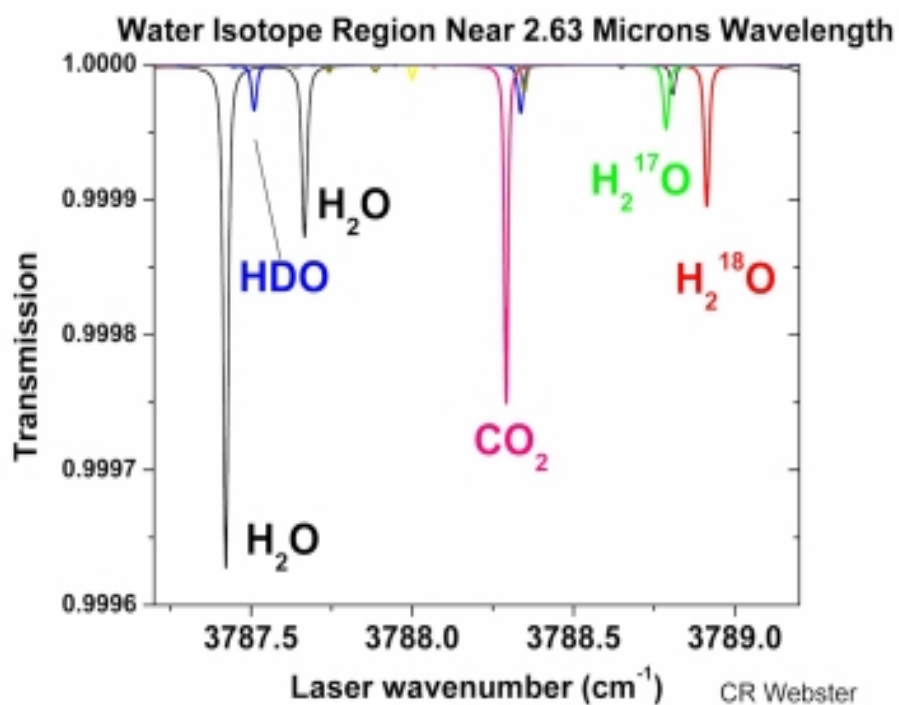
# Near-IR and Mid-IR Spectroscopy of Water Isotopes $\text{H}_2\text{O}$ , $\text{HDO}$ , $\text{H}_2^{18}\text{O}$ , $\text{H}_2^{17}\text{O}$

Near-IR 2.63  $\mu\text{m}$

$\text{HDO}$  linestrength  $\rightarrow \times 2$

Mid-IR 6.7  $\mu\text{m}$

- Near-IR lines weaker than Mid-IR, and have stronger interferences from  $\text{CO}_2$ , other gases
- Unlike Mid-IR, Near-IR offers  $\text{CO}_2$  normalization



# Mid-IR Measurements of Water Isotopes

## $\text{H}_2\text{O}$ , $\text{HDO}$ , $\text{H}_2^{18}\text{O}$ , $\text{H}_2^{17}\text{O}$

- Region first identified by Rinsland *et al.* 1984 balloon measurements of HDO.
- ATMOS studied lower stratosphere.
- BLISS made first *in situ* TDL measurements in 1989.
- WISP developed for WB57-F, but only flown in test flight with no lasers.
- Community awaits *in situ* measurements near tropopause region at high spatial resolution: uncertainty in measured T  $\sim 1\%$  at night.

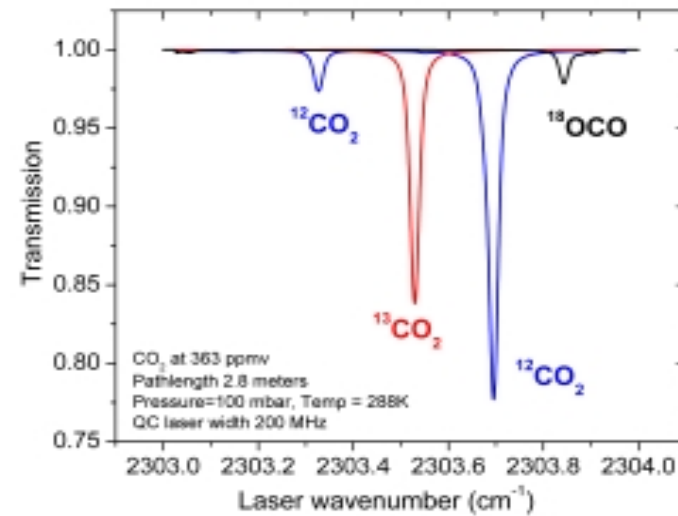
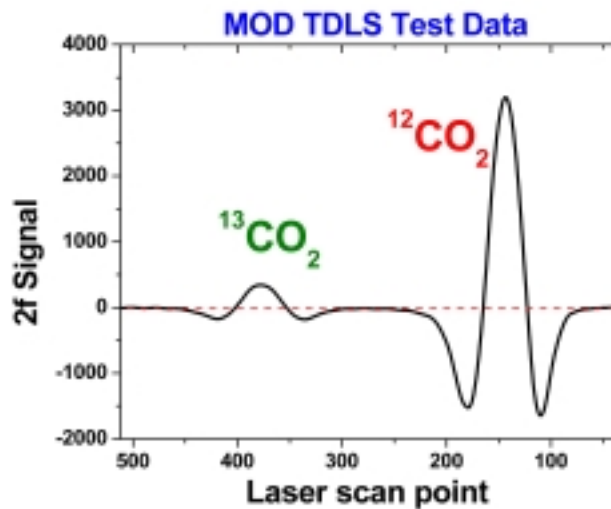
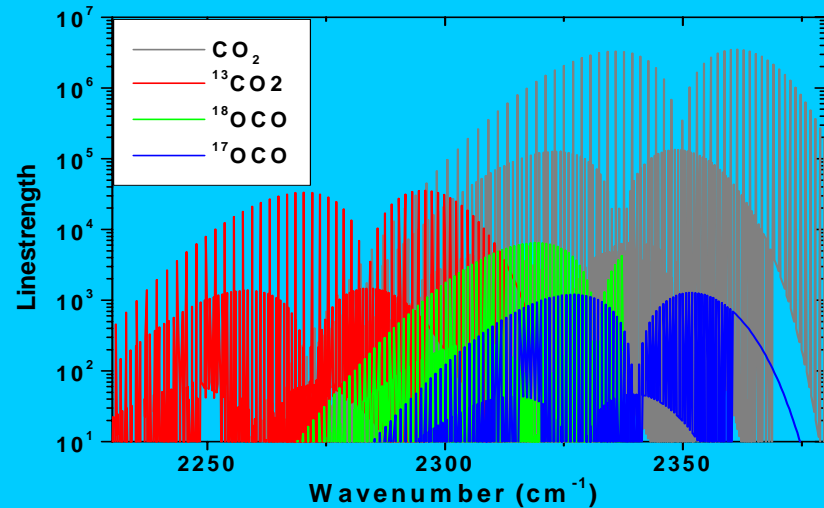
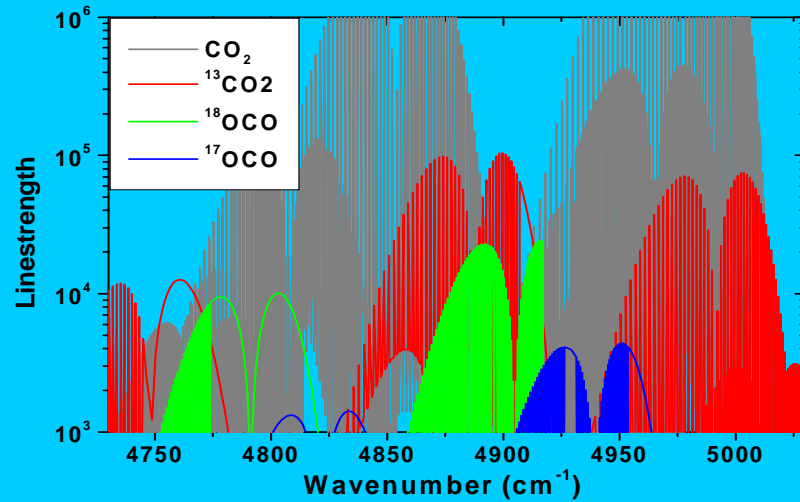
Water Isotope Ratio Measurement Error from Temp Uncertainty of 2 Degrees							
Water mixing-ratio (ppmv)				5	50	200	
CH4 mixing-ratio (ppmv)				0.8	1.0	1.5	
Atmospheric Temp (K)				210 K	198 K	245 K	
Atmospheric Pressure (mbar)				60 mbar	100 mbar	300 mbar	
					Error % from +2 deg error in Temp		
Species	$\nu$ ( $\text{cm}^{-1}$ )	S (296 K)	$E''$ ( $\text{cm}^{-1}$ )	n ( $\text{cm}^{-1}$ )			
CH4	1483.79230	3.65E-22	157	0.75	-0.6		
CH4	1483.83448	2.29E-22	157	0.75			
H218O	1483.92606	8.39E-23	550	0.49	+0.5	+0.6	+0.4
HDO	1484.10644	2.32E-23	226	0.74	<0.1	<0.1	<0.1
H2O	1484.25726	1.78E-23	1899	0.50	Too weak		
H217O	1484.51094	1.97E-23	205	0.59	<0.1	-0.1	-0.4
H218O	1485.13361	6.25E-23	1907	0.78	+0.5	+0.6	+0.5
(HDO/H217O)					<1 per mil	<1 per mil	4 per mil

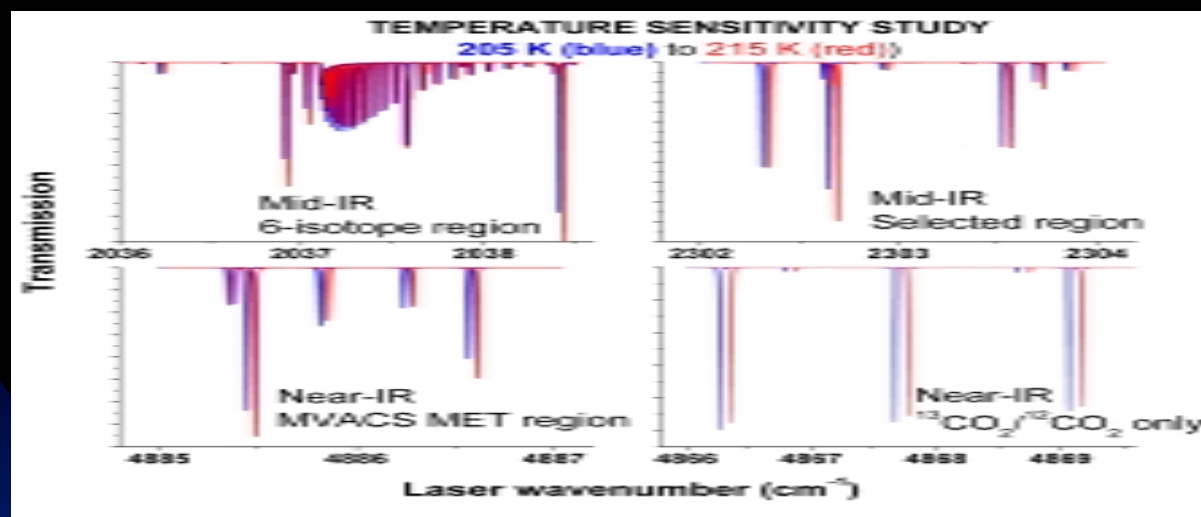
# Near-IR and Mid-IR Isotopic CO<sub>2</sub>

Near-IR 2.05  $\mu\text{m}$

Linestrength  $\rightarrow \times 2000$

Mid-IR 4.24  $\mu\text{m}$



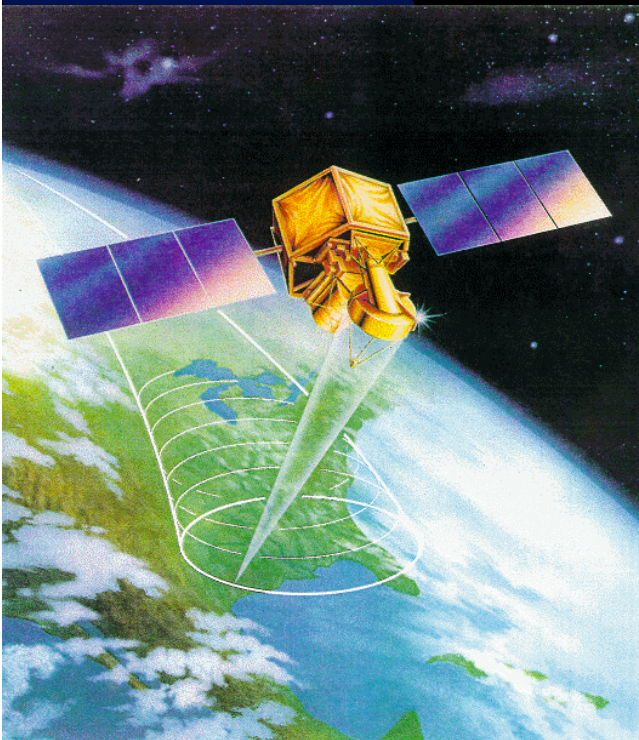


SPECTRAL REGION	$^{13}\text{CO}_2/\text{CO}_2$	$^{18}\text{OCO}/\text{CO}_2$
Near-IR MET TDLS 4886 $\text{cm}^{-1}$	-24 per mil/deg K	+19 per mil/deg K
Near-IR TEGA TDLS 4876 $\text{cm}^{-1}$	-6 per mil/deg K	TBD
Near-IR 4868 $\text{cm}^{-1}$	+1 per mil/deg K (but dynamic range may limit to 5 per mil total).	Not possible
Mid-IR QCLS strong region at 2302 $\text{cm}^{-1}$	-2 per mil/deg K	-1 per mil/deg K
Mid-IR QCLS special 6- isotope region at 2037 $\text{cm}^{-1}$	-1 per mil/deg K, but can fit temp from Q- branch	TDB



# Near-IR Laser Absorption Spectrometer for Global CO<sub>2</sub> Mapping

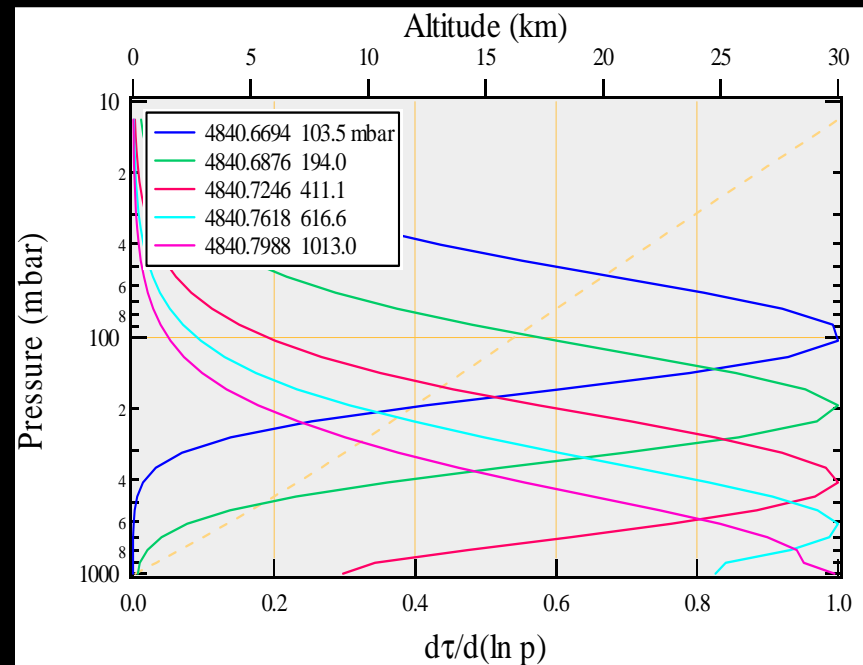
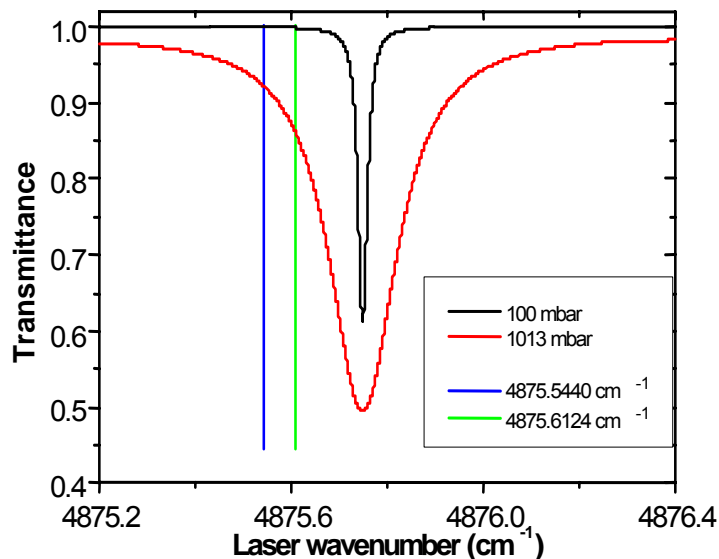
**JPL: Robert Menzies (PI), Chris Webster, David Tratt, Gary Spiers**  
**Colorado State Univ.: Graeme Stevens**  
**Coherent Technologies: Mark Philips**



- Near-nadir cw laser (rare-Earth ion doped) illumination of Earth's surface from orbit.
- Analysis of integrated path differential absorption at selected transmit frequencies within CO<sub>2</sub> absorption line region to retrieve tropospheric CO<sub>2</sub> profiles.
- Retrieval of CO<sub>2</sub> profiles in lower and middle troposphere by differential absorption in column above land or ocean backscattering surface.
  - Need column to 1-2 ppmv (0.3%) to define spatial gradients.
  - Code Y IIP funded for DC-8 demonstration (2003).

# Near-IR Laser Absorption Spectrometer for Global CO<sub>2</sub> Mapping

- Two near-IR regions suitable for satellite measurements of global CO<sub>2</sub> column
  - 1.57  $\mu\text{m}$  (30012  $\leftarrow$  00001) band  
*[Chip Miller, Linda Brown: sharper cores and stronger wings: 2 Voigts reqd.]*
  - 2.05  $\mu\text{m}$  (30013  $\leftarrow$  00001) band
- Optimal combination of optical depth, insensitivity to temperature, and no interferences.





# Outlook for TDL and QC *in situ* Laser Spectrometers

**TDL and QC LAS offer excellent sensitivity, specificity, precision, and response time, especially for small molecules.**

- As *in situ* Earth instrument capability has evolved with aircraft missions, laser spectrometers have a more focused niche: H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>4</sub>, CO, HCl, isotopic measurements, H<sub>2</sub>CO
  - CO<sub>2</sub> better done with IR absorption (4.3 μm) LiCor NDIR (Wofsy, Sachse, Avallone, etc.): precision 0.01%, accuracy 0.03%.
  - LIF better for radicals OH, NO<sub>2</sub>, ClONO<sub>2</sub>, ClO, Cl<sub>2</sub>O<sub>2</sub>, etc.
  - CRDS detection has potential for improved precision, but test flight data (CH<sub>4</sub> precision 0.3%) achieved in 10 sec compare to 1.3 sec for conventional LAS.
- *In situ* laser spectrometers for all gases including H<sub>2</sub>O will soon be based on mid-IR room temperature cw QC lasers with HgCdTeZn room temperature detectors.
  - For H<sub>2</sub>O, enormous flight heritage of Near-IR instruments, and excellent InGaAs detectors will delay transition.

# Specific Spectroscopic Measurement Needs – Near-IR

## H<sub>2</sub>O:

- Immediate need for H<sub>2</sub>O in Near-IR 1.37  $\mu\text{m}$  region for 8 existing, flight-tested aircraft and balloon instruments.
- Hitran2000: strong lines targeted by instruments rely on outdated incorrect (?) measurements!
- Linestrengths, FBC, temp dependences, pressure shifts, partition functions.

## CO<sub>2</sub>:

- Long-term need for Near-IR CO<sub>2</sub> region for global CO<sub>2</sub> LAS measurements. Two near-IR regions suitable for satellite measurements of global CO<sub>2</sub> column
  - 1.57  $\mu\text{m}$  (30012 <- 00001) band
  - 2.05  $\mu\text{m}$  (30013 <- 00001) band
- All parameters important, including line shifts.

Water isotopes H<sub>2</sub>O, HDO, H<sub>2</sub><sup>18</sup>O at 2.7  $\mu\text{m}$  better measured in mid-IR.

CH<sub>4</sub>: better measured in mid-IR.

# Specific Spectroscopic Measurement Needs – Mid-IR

- Tracer gases  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$ 
  - Better Lorentz broadening coefficients and temp dependence for  $\text{CH}_4$  ( $\nu_3$ ),  $\text{N}_2\text{O}$  ( $\nu_3$ ), and  $\text{CO}$  fundamental, better partition functions for temp corrections.
- Reactive gases  $\text{HCl}$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{CO}$ , etc
  - $\text{HCl}$  well-measured
  - Linestrengths and broadening coefficients needed for  $\text{H}_2\text{CO}$  at  $1740\text{ cm}^{-1}$  (Zahniser/Brown?)
- Isotopic species:
  - Water isotopes
  - $\text{CO}_2$  isotopes
  - $\text{CH}_4$  isotopes,  $\text{N}_2\text{O}$  isotopes,  $\text{CO}$  isotopes